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Hanson, H.; Dekker, A. J.; van der Woude, F.

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Analysis of the pitch in binary cholesteric liquid crystal mixtures

H. Hanson, A. J. Dekker, and F. van der Woude

Solid State Physics Laboratory, Materials Science Center, University of Groningen, Groningen, The Netherlands
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The pitch p in the cholesteric liquid crystal phase of mixtures of cholesteryl chloride and p -azoxyanisole has been measured as a function of the composition c . The function $p^{-1}(c)$ deviates considerably from linearity and shows an inversion of the helical twist sense. The results, as well as those of five other binary cholesteric systems published in the literature, have been analyzed in terms of the molecular theory of Goossens. In the discussion of the results of the analysis, the requirements for a consistent physical interpretation of the interaction parameters that appear in the theory have been emphasized. The results indicate that these requirements are satisfied only in simple systems that do not deviate strongly from linear behavior of $p^{-1}(c)$. In more complicated systems the specific properties of the individual molecules probably play an important role in determining the cholesteric helix.

I. INTRODUCTION

The pitch p of the helix of a cholesteric liquid crystal can be varied in several ways; for example by adding solvents or nematic materials to a cholesteric, or by adding optically active molecules to a nematic, or by mixing cholesteric substances. The properties of these mixtures are sometimes intermediate between those of the components, but if the components are chemically dissimilar, these properties may vary in a nonlinear fashion with composition in a seemingly unpredictable manner.

It is well known that a mixture of a right- and left-handed cholesteric exhibits inversion of the rotation sense of the helix as one passes through a critical composition that corresponds to a compensated nematic state. Perhaps more surprising is helix inversion in a cholesteric-nematic system or in a mixture of two cholesterics with the same helix screw sense in the pure state. Evidence for helix inversion in a mixture of nematic MBBA (p -methoxybenzylidene- p - n -butylaniline) and cholesteric cholesteryl chloride has been obtained by Saeva and Wysocki¹ from measurements of the wavelength for maximum reflection, $\lambda_0 = np$ (where n is the mean index of refraction). In similar measurements, Finkelmann and Stegemeyer² observed an inversion and even a twofold inversion of the helical twist in some binary cholesteric mixtures. Stegemeyer and Finkelmann³ analyzed their data in terms of the molecular theory of Goossens,⁴ which will be discussed below.

In order to provide further experimental information to test Goossens's theory we carried out pitch measurements in binary mixtures of cholesteric cholesteryl chloride (CC) and nematic p -azoxyanisole (PAA); this system also exhibits inversion of the helical screw sense. For the purpose of analyzing the experimental results we adapted the theory of Goossens, to provide a formula for the pitch of a binary cholesteric system in terms of the intermolecular interaction parameters and composition. These interaction parameters were obtained by a least square computer fit of the theoretical expression to all measured points.

We also analyzed in a similar manner the experimental reciprocal pitch versus composition curves for five binary cholesteric mixtures published by other investiga-

tors. Among them are three systems that were analyzed before by Stegemeyer and Finkelmann.³ Our results differ appreciably from theirs because they introduced some unwarranted approximations and employed only a few special points of each curve.

In the discussion of our analysis we emphasize the requirements for an internally consistent physical interpretation of the interaction coefficients in the theory of Goossens. It turns out that these are met only in relatively simple mixtures for which the deviations from linear behavior are not too large. In more complicated situations it seems likely that local intermolecular interactions, not included in the general approach of Goossens, may be of importance in determining the helical structure. Such interactions may refer, for example, to the specific shapes and sizes of the individual molecules.

II. EXPERIMENTAL RESULTS

In mixtures of nematic PAA and cholesteric CC we measured the pitch p as a function of composition with the "variable wedge" method of Grandjean-Cano.⁵ The sense of rotation of the helix was obtained by observation of the optical rotation of a linearly polarized wave. In our case $\lambda < |p|$, so that the spiral formed by the plane of polarization as the linearly polarized wave propagates through the medium has a sense of rotation opposite to that of the cholesteric helix.⁶ For a helix with a right-handed screw $p > 0$; for a left-handed helix $p < 0$.

PAA has a nematic mesophase between 118 and 134 °C; the compound CC has a monotropic cholesteric phase below 65 °C, i. e., it can only be obtained by supercooling below the crystalline-isotropic transition temperature of 95 °C. All mixtures were monotropic too. The twist angle θ between the directors of two nematic layers separated by a distance y parallel to the helical axis is related to the pitch by $\theta = 2\pi y/p$. Since $d\theta/dy$ plays an important role in the results of Goossens's theory, we present our data in terms of the so-called helical twisting power p^{-1} . Figure 1 shows p^{-1} of the PAA-CC mixtures as a function of c , the mole fraction of CC. The curve does not represent an isotherm but refers to temperatures 5° below the cholesteric-isotropic transition temperature for each composition. A mixture of PAA with a small amount of CC gives a cholesteric liquid

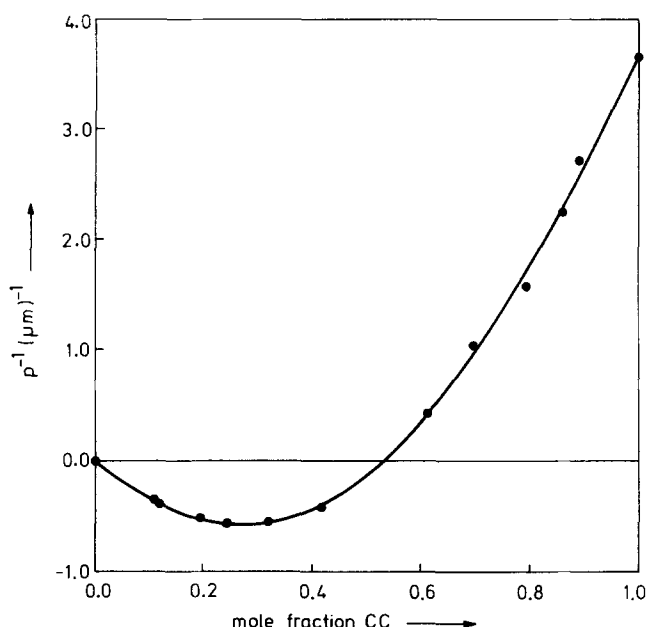


FIG. 1. Experimental results for the reciprocal cholesteric pitch of mixtures of *p*-azoxyanisole and cholesteryl chloride, measured at $(T_c - 5)$ K.

crystal with a left-handed helical structure. With increasing concentration of CC, p^{-1} first decreases to a minimum and then increases to become zero at $c = 0.52$. This implies that for this composition and for the specific temperature $(T_c - 5)$ the mixture is nematic. Further increase of the CC concentration yields a cholesteric with a right-handed helical structure.

III. BASIS OF ANALYSIS

Our analysis of binary cholesteric mixtures is based on the theory of Goossens,⁴ which can be considered as an extension of the molecular statistical theory of Maier and Saupe⁷ for nematic liquid crystals. To elucidate the physical origin of the twist in cholesteric systems according to the interpretation proposed by Goossens, we give here a qualitative summary of its essentials. The starting point is the second order perturbation expression for the dispersion energy between two neutral molecules i and j ,

$$V_{ij} = - \sum_{n_i, n_j} \frac{\langle 0_i, 0_j | H_{ij} | n_i, n_j \rangle \langle n_i, n_j | H_{ij} | 0_i, 0_j \rangle}{E_{n_i, n_j} - E_{0_i, 0_j}} \quad (1)$$

n_i, n_j refer to excited states and $0_i, 0_j$ to the ground states. Representing the molecules by systems of point charges e_{ik} and e_{jl} , the electrostatic interaction Hamiltonian is

$$H_{ij} = \sum_{k,l} \frac{e_{ik} e_{jl}}{|\mathbf{r}_i + \rho_{ik} - (\mathbf{r}_j + \rho_{jl})|}, \quad (2)$$

where ρ_{ik} and ρ_{jl} denote the positions of the charges relative to the origins of the molecular coordinate systems located at \mathbf{r}_i and \mathbf{r}_j . Dipole and quadrupole components in an excited state are represented, respectively, by

$$p_{ix} = \sum_k e_{ik} \rho_{ikx}, \text{ etc. and } q_{ixy} = \sum_k e_{ik} \rho_{ikx} \rho_{iky}, \text{ etc.}$$

The first two terms of an expansion of H_{ij} in powers of $1/r \equiv 1/|\mathbf{r}_i - \mathbf{r}_j|$ are of dipole-dipole character ($\approx p_i p_j / r^3$) and of dipole-quadrupole character [$\approx (p_i q_j + q_i p_j) / r^4$], i. e.,

$$H_{ij} = H_{p_i p_j} + (H_{p_i q_j} + H_{q_i p_j}) + \dots \quad (3)$$

Higher order terms are neglected. In V_{ij} this leads to terms that are quadratic in the dipole-dipole interaction ($\approx -p_i^2 p_j^2 / E_{n_i, n_j}$) and to mixed terms consisting of products of dipole-dipole and dipole-quadrupole interactions [$\approx - (p_i^2 p_j q_j + p_i q_i p_j^2) / E_{n_i, n_j}$]. Thus, V_{ij} can be represented symbolically by

$$V_{ij} = V_{p_i^2 p_j^2} + (V_{p_i^2 p_j q_j} + V_{p_i q_i p_j^2}). \quad (4)$$

Maier and Saupe⁷ only retained the first term of V_{ij} . Since $p_i^2 / E_{n_i, n_j}$ essentially represents a polarizability α_i and p_j^2 / r^6 is a measure for the mean square field F_{ij}^2 produced by j at the location of i , the quantity $V_{p_i^2 p_j^2}$ may be interpreted as $-\frac{1}{2} \alpha_i F_{ij}^2$, i. e., as the energy of α_i in the mean square field produced by j . Now, in the local field approximation of Maier-Saupe for nematics, based on anisotropic molecules, the anisotropic part of F_i^2 produced by all other molecules j at the location of i lies along the nematic axis. If the long axis (of highest polarizability) of i makes an angle θ_i with the nematic axis, the energy of this molecule V_i in the mean square local field will contain a term proportional to $-F_i^2 \cos^2 \theta_i$, or to $-F_i^2 \cos 2\theta_i$. This forms the physical basis for the tendency of parallel alignment in the Maier-Saupe treatment of nematics. This tendency is, of course, retained in the theory of Goossens for cholesteric systems; the important contribution of Goossens is, however, that he showed that the mixed terms in V_{ij} can give rise to the twist in these systems. For this purpose he used a local field approximation compatible with the symmetry of cholesteric systems, which he considered as nematic planes ($\parallel x-z$ plane) stacked along the y axis. Goossens then calculates the dispersion energy between a molecule i in nematic plane (a) and a molecule j in a neighboring nematic plane (b), averaged over all positions and over four distinct orientations of the molecular axes in the planes. In terms of the angle $\theta_{ab} (= -\theta_{ba})$ between the long molecular ζ axes in these planes, Goossens's result, when applied to a binary mixture of molecules of types 1 and 2, yields for the dispersion energy V_{ab} between planes (a) and (b) per unit area

$$V_{ab} = - (3/16 y_{ab}^4) (A_{11} \nu_1^2 + 2A_{12} \nu_1 \nu_2 + A_{22} \nu_2^2) \cos 2\theta_{ab} + (2/y_{ab}) [B_{11} \nu_1^2 + (B_{12} + B_{21}) \nu_1 \nu_2 + B_{22} \nu_2^2] \sin 2\theta_{ab}. \quad (5)$$

Here $y_{ab} = y_a - y_b = -y_{ba}$ is the separation between the nematic planes measured along the cholesteric y axis; ν_1 and ν_2 represent the number of molecules of each type per unit area in a nematic plane. The molecular quantities A_{ij} and B_{ij} contain matrix elements expressed in the molecular coordinates ξ, η, ζ ,

$$A_{ij} = \sum_{n_i, n_j} \frac{(p_\xi^2 - p_\eta^2)_{0_i, n_i} (p_\xi^2 - p_\eta^2)_{0_j, n_j}}{4(E_{n_i, n_j} - E_{0_i, 0_j})} \quad (6a)$$

$$B_{ij} = \sum_{n_i, n_j} \frac{(p_\xi^2 - p_\eta^2)_{0_i, n_i} (p_\xi q_{\xi\eta} + p_\eta q_{\eta\xi} + \text{c. c.})_{0_j, n_j}}{2(E_{n_i, n_j} - E_{0_i, 0_j})} \quad (6b)$$

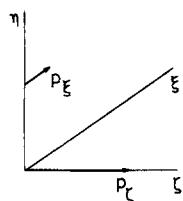


FIG. 2. Coupled harmonic oscillator model for an optically active molecule according to Kuhn.⁸

Note that $A_{ij} = A_{ji}$ but $B_{ij} \neq B_{ji}$. The term in (5) containing $\cos 2\theta_{ab}$ has Maier-Saupe character; it arises from the tendency for parallel orientation of the long ζ axes of anisotropic molecules. For the interpretation of the asymmetric term containing $\sin 2\theta_{ab}$ it is important to realize that the matrix elements $p_j q_i$ only appear in the form $p_\zeta q_{\eta}$ or cyclic permutations. This implies that a dipole moment p_ζ induced along the ζ axis must be accompanied by a nonvanishing quadrupole component in the ξ - η plane. This requires lack of a center or plane of symmetry. In fact, the simplest molecular model compatible with these requirements consists of a dipole p_ζ induced along the ζ axis coupled with an induced dipole moment p_η in a point $\eta \neq 0$, as indicated in Fig. 2. This model of two harmonic oscillators coupled in a particular phase relation is actually reminiscent of the old Kuhn model for optically active molecules.⁸ Since for an optically active molecule in plane (b) both the oscillator along the ζ axis and the phase-coupled oscillator along the ξ axis tend to align along the mean square field along the nematic axis of plane (a), this model elucidates the physical origin of the cholesteric twist.

In order to obtain from (5) a basis for analysis of experimental results for binary mixtures it is necessary to express V_{ab} in terms of the molecular concentrations c_1 and $c_2 = (1 - c_1)$ of the components. For this purpose we are practically compelled to introduce the simplifying assumption that the effective thickness y_{ab} is the same for both kinds of molecules at a particular composition. When Ω_1 and Ω_2 represent the effective volumes per molecule, the surface densities ν_1 and ν_2 expressed in terms of the molecular concentrations are then $\nu_1 = c_1 y_{ab} / (c_1 \Omega_1 + c_2 \Omega_2)$ and $\nu_2 = c_2 y_{ab} / (c_1 \Omega_1 + c_2 \Omega_2)$. Under these conditions we can write (5) in the form

$$V_{ab} = -(3/16 y_{ab}^2) (c_1 \Omega_1 + c_2 \Omega_2)^{-2} \{ (A_{11} c_1^2 + 2A_{12} c_1 c_2 + A_{22} c_2^2) \cos 2\theta_{ab} + (2/y_{ab}) [B_{11} c_1^2 + (B_{12} + B_{21}) c_1 c_2 + B_{22} c_2^2] \sin 2\theta_{ab} \}. \quad (7)$$

Minimizing V_{ab} with respect to the twist angle θ_{ab} one obtains

$$2\theta_{ab} \approx \tan 2\theta_{ab} = \frac{2}{y_{ab}} \frac{(B_{11} - B_{12} - B_{21} + B_{22}) c_1^2 + (B_{12} + B_{21} - 2B_{22}) c_1 + B_{22}}{(A_{11} - 2A_{12} + A_{22}) c_1^2 + 2(A_{12} - A_{22}) c_1 + A_{22}}. \quad (8)$$

Although in the present approximation θ_{ab} is not affected by the variation of the molecular volume described by the factor $(c_1 \Omega_1 + c_2 \Omega_2)^{-2}$, this factor will influence the variation of the critical temperature with composition because it depends essentially on the coefficient of $\cos 2\theta_{ab}$ in (7).

Unless one knows y_{ab} , a fit of the reciprocal pitch $1/p$

$= (1/2\pi)(d\theta/dy) = (1/2\pi)(\theta_{ab}/y_{ab})$ versus composition curve only allows the determination of the ratio's between the A_{ij} 's and between the B_{ij} 's.

Finally, one should realize that Goossens's theory is based on an ideal model of a cholesteric. The "molecular" quantities A_{ij} and B_{ij} obtained from an analysis of experimental results of course include the order parameters of the two kinds of molecules; in general these will depend on temperature and composition.

IV. RESULTS OF ANALYSIS AND DISCUSSION

A. Special cases

As a guideline for the discussion of the results of our analysis of experimental data in terms of Goossens's theory we first consider some special cases of expression (8). For this purpose we shall assume that the effective thickness per molecule, y_{ab} , is independent of composition.

(a) The simplest hypothetical binary cholesteric system would consist of cholesteric and nematic molecules that differ from each other only by the presence of an optically active center in the former that is lacking in the latter. Since according to (6) an interaction coefficient A_{ij} is essentially determined by the product $(\alpha_i \alpha_j)$ of the anisotropic parts of the polarizabilities of the two molecules involved, one expects in this case $A_{11} \approx A_{22} \approx A_{12} \approx A$. This would remain true even if the partial order parameters were included. Similarly, since B_{ij} has essentially $\alpha_i(p_j q_i)$ character, $B_{21} \approx B_{11} \approx B$. Since furthermore $B_{22} = B_{12} = 0$ because component 2 is nematic, (8) reduces to

$$\theta_{ab} \approx B c_1 / A y_{ab}, \quad (9)$$

i. e. the twist angle per nematic layer is simply proportional to the concentration of the cholesteric component.

In this connection it is interesting to mention that Pochan and Hinman⁸ recently reported such a linear behavior for the system consisting of cholesteric cholesteryl 2-propyn-1-yl carbonate (CPC) and nematic MBBA. This system provides apparently an example of (9), even though the two components are chemically dissimilar.

(b) Another simple hypothetical system would consist of two similar kinds of cholesteric molecules which differ only in their optically active centers. For such a system we would again have $A_{11} \approx A_{22} \approx A_{12} = A$ and furthermore $B_{21} \approx B_{11}$ and $B_{12} \approx B_{22}$. In this case (8) also reduces to a twist angle which varies linearly with composition,

$$\theta_{ab} = (B_{11} c_1 + B_{22} c_2) / A y_{ab}. \quad (10)$$

B_{11} and B_{22} do not necessarily have the same sign. Examples of systems that satisfy (10) reasonably well are mixtures of cholesteryl oleyl carbonate (COC) and cholesteryl halides for which measurements of the wavelength for maximum reflection have been carried out by Leder.¹⁰

A special case that arises in this category is a mixture of the left- and right-handed species of a single compound; in that case $B_{11} = -B_{22}$ and (10) becomes

TABLE I. Ratios of molecular quantities obtained from analysis of the experimental results by means of the theory of Goossens (Ref. 4). Values in parentheses are results of Stegemeyer and Finkelmann (Ref. 3). (CC=cholesteryl chloride, PAA=*p*-azoxyanisole, CP=cholesteryl propionate, MBA=*p*-methoxybenzylidene-*p*-amino phenylacetate, CEEC=cholesteryl 2-(ethoxy ethoxy) ethyl carbonate, EBBA=(*p*-ethoxy benzylidene)-*p*-*n*-butylaniline, MBBA=(*p*-methoxybenzylidene)-*p*-*n*-butylaniline, CBAC=amyl-*p*-(4 cyanobenzylidene amino)-cinnamate.)

Compound 1	Compound 2	$\frac{A_{11}}{A_{22}}$	$\frac{A_{12}}{A_{22}}$	$\frac{B_{22}}{B_{11}}$	$\frac{B_{21}}{B_{11}}$	$\frac{B_{21} + B_{12}}{2B_{11}}$
CC	PAA	0.98	0.82	0	-1.12	
CP	MBA	1.7	1.2	0	1.8	(Ref. 12)
CEEC	EBBA	1.64	0.66	0	-10.3	(Ref. 2)
CC	MBBA	1.62	1.04	0	-1.58	(Ref. 1)
CEEC	CBAC	1.51	0.90	2.71(3.95)		-5.34(-16.0) (Ref. 2)
CC	CBAC	1.2	1.2	0.61(0.74)		-0.18(-0.068) (Ref. 3)

$$\theta_{ab} = B_{11}(2c_1 - 1)/A_{yab}. \quad (11)$$

This behavior has indeed been found experimentally by Dolphin *et al.*¹¹ for *p*-ethoxybenzal-*p*-(β -methylbutyl) aniline (EBMBA) for the whole temperature range of the mesophase.

(c) Next in line of increasing complexity are binary mixtures of a cholesteric and a chemically dissimilar nematic. The system cholesteryl chloride (CC) and *p*-azoxyanisole (PAA) for which our pitch measurements are presented in Fig. 1 belongs in this category. The experimental values obtained for $1/p$ as a function of composition were analyzed by a least square computer fit to the function

$$\frac{1}{p} = \frac{a_1 c_1^2 + a_2 c_1 + a_3}{a_4 c_1^2 + a_5 c_1 + 1}. \quad (12)$$

From the a_i values so obtained, the ratios between the A_{ij} 's and B_{ij} 's were calculated by employing the relation $\theta_{ab} = 2\pi y_{ab}/p$ between (8) and (12). The results for the system CC-PAA are included in Table I, since PAA is nematic, $B_{22} = B_{12} = 0$ in this case. This table also includes results for five other systems that were analyzed in a similar manner; three of them fall in the present category. The experimental curves for these five systems are reproduced in Fig. 3.

(d) Finally, mixtures of two different cholesteric materials form the most general application of expression (8); results of the analysis of two such systems are included in Table I.

B. Comments on numerical results

Before commenting on the results of our analysis it may be in order to provide an estimate of the errors involved in the numerical values of the ratios given in Table I. For this purpose computer simulations were carried out for various cases. From the results obtained we conclude that for the systems that exhibit inversion of the helical twist sense (CC-PAA; CEEC-EBBA; CC-MBBA, and CEEC-CBAC) the errors in the ratios between the B_{ij} are only of the order of a few percent. For the other two systems (CP-MBA and CC-CBAC) the errors in the ratios between the B_{ij} are considerably larger, say about 15%. For the ratios between the A_{ij}

the errors are estimated to lie between 5 and 20% in the systems studied.

With regard to the values for the ratios between the interaction coefficients A_{ij} presented in Table I, we wish to point out that if these quantities were truly *molecular* quantities, one might expect them to satisfy the approximate relation $A_{12}^2 \approx A_{11}A_{22}$. This follows immediately from the physical interpretation of the A_{ij} 's mentioned under (a) above. Deviations might of course be expected, for example, if the partial order parameters S_i and S_j depend appreciably on composition at the temperatures to which the pitch measurements refer, because A_{ij} should more realistically be interpreted as $(\alpha_i S_i)(\alpha_j S_j)$. In any case, we note that the required relation is satisfied approximately only by the systems CP-MBA and CC-CBAC in Table I; the other four systems show considerable deviations from this relation.

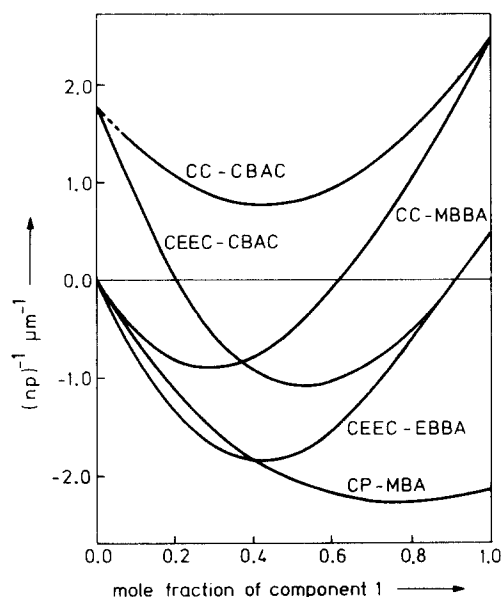


FIG. 3. Experimental curves for the reciprocal of the wavelength of maximum reflection, $\lambda_0^{-1} = (np)^{-1}$, as a function of composition for five binary cholesteric mixtures taken from the literature; n is the mean index of refraction and p the cholesteric pitch. For references and a legend to the abbreviations see Table I.

We further observe from Table I that in all systems, except CP-MBA, the mixed coefficients $\frac{1}{2}(B_{21} + B_{12})$ (or in cholesteric-nematic mixtures B_{21}) have a sign opposite to that of B_{11} and B_{22} . In this respect it is perhaps interesting to note that the cholesteric compound in the CP-MBA system is the only one with a left-handed helical screw sense; in the remaining five systems the pure cholesteric components exhibit a right-handed helical screw. A negative B_{21}/B_{11} ratio in a cholesteric-nematic system implies that a cholesteric molecule in a nematic environment tends to turn its long axis relative to the preferred direction in an adjacent plane through an angle opposite in sign to that of a cholesteric molecule in an environment of similar cholesteric molecules. For low concentrations of the cholesteric component, the twist angle is caused largely by the $(pq)_{\text{chol}}(p^2)_{\text{nem}}$ interaction between a cholesteric molecule and the nematic matrix. The twist is then determined by the molecular properties of a "free" cholesteric molecule. For compositions in which the cholesteric component is present in large concentrations, the intermolecular interaction between cholesteric molecules becomes predominant in determining the twist. When the latter has a sign opposite to that of the dilute case, one can understand qualitatively the occurrence of an extremum in the θ versus composition curve and the inversion of the helical twist sense. This is presumably the case in the systems CC-PAA, CEEC-EBBA (for which B_{21}/B_{11} has the strikingly large value ~ 10.3), and CC-MBBA. However, in terms of a physical interpretation of B_{21} as an interaction of $(p^2)_{\text{nem}}(pq)_{\text{chol}}$ character and B_{11} as an interaction of $(p^2)_{\text{chol}}(pq)_{\text{chol}}$ character, a negative sign of B_{21}/B_{11} seems unintelligible. It would appear, in fact, that these results indicate the importance of the specific shape of the individual molecules in determining the cholesteric structure. Such effects are of course not included in the general approach used by Goossens.

In mixtures of two cholesteric substances which in the pure state have the same helical screw sense (systems CEEC-CBAC and CC-CBAC), a negative value of $\frac{1}{2}(B_{21} + B_{12})/B_{11}$ implies that the twisting power of a cholesteric molecule in an environment of similar molecules has a sign opposite to that in an environment of the other kind of molecules. When $\frac{1}{2}|B_{21} + B_{12}|$ is large enough relative to B_{11} and B_{22} , one expects a twofold inversion of the helical screw sense. In fact, if one puts $\theta_{ab} = 0$ in (8) we find that inversion will occur only if $\frac{1}{2}|B_{21} + B_{12}| > |B_{11}B_{22}|^{1/2}$. Here, the same difficulty as in cholesteric-nematic mixtures is encountered with regard to the physical understanding of a negative sign in terms of Goossen's theory.

Disregarding the signs of the coefficients B_{ij} , one might also expect from the physical interpretation of the A_{ij} and B_{ij} that $|B_{21}/B_{11}| \approx A_{21}/A_{11}$. Apart from the systems CC-PAA, this relation is not even approximately satisfied by any of the other mixtures collected in Table I. This again indicates the possible importance of specific interactions between the molecules which are not included in the theory of Goossens.

In order to obtain an order of magnitude for a ratio like B_{11}/A_{11} we take for a typical case $y_{ab} \approx 5 \text{ \AA}$, $p \approx 0.3$

μm , $c_1 = 1$ and find from (8) and from $\theta_{ab} = (2\pi/p)y_{ab}$ the value $B_{11}/A_{11} \approx 0.05 \text{ \AA}$.

C. Other analyses

Stegemeyer and Finkelmann³ also analyzed their experimental data in terms of the theory of Goossens; their results for B_{22}/B_{11} and B_{12}/B_{11} for three systems are included in Table I. They did not carry out a computer analysis to fit (8) to all experimental points; instead, they only employed the information provided by the helical inversion points, the extrema and the end points of the curves. Furthermore, in their mathematical handling of this information they introduced some unwarranted simplifying assumptions. These can be traced, in fact, to the assumption that the denominator in (8) does not vary with composition, i.e., to the assumption $A_{11} = A_{22} = A_{12}$. This explains the discrepancies between their values for B_{22}/B_{11} and B_{12}/B_{11} and ours, which were obtained by a computer fit to all experimental points.

Adams *et al.*¹³ recently reported a phenomenological treatment of the dependence of the pitch on composition in mixtures of liquid crystals. They assert that the wavelength of maximum reflection, λ_m , in binary cholesteric systems can be described satisfactorily by an empirical formula of the form

$$1/\lambda_m = (w_1/\lambda_1) + (w_2/\lambda_2) + Kw_1w_2, \quad (13)$$

where λ_1 and λ_2 refer to the reflection wavelengths of the pure components; w_1 and w_2 refer to the weight percentages and K is a parameter that is adjusted to fit the experimental curve. This "single parameter" representation is mathematically similar to the Stegemeyer-Finkelmann analysis, because in both cases the experimental curves are fitted to a simple quadratic function of the relative amount of one of the components. The difference between the two lies in the use of weight (or, nearly equivalently, volume) percentages by Adams *et al.* and molecular concentrations by Stegemeyer and Finkelmann. Furthermore, the latter authors employed Goossen's theory as a starting point, and consequently, their interpretation would be more specific than that of Adams *et al.*

We also attempted a least square computer fit of the experimental data for the systems considered in the present paper to formula (13) and found that the computed curves showed systematic deviations from the experimental data. This indicates in our opinion that (13), in contrast to (12), does not contain enough adjustable parameters to provide a mathematically satisfactory representation of the data. This conclusion is supported by the fact that the estimated errors in the ratios of the A_{ij} in our own analysis are less than 20%.

D. Concluding remarks

From our analysis we conclude that the molecular theory of Goossens provides a mathematically satisfactory description of the observed dependence of the pitch of binary cholesteric mixtures on composition. How-

ever, only simple systems, for which the reciprocal pitch versus composition relation does not deviate strongly from linearity, allow a consistent physical interpretation of the intermolecular interaction parameters. In more complicated systems, such as those which exhibit inversion of the helix screw sense, local intermolecular interactions not included in the general approach of Goossens probably play an important role in determining the structure of the cholesteric helix. Such local interactions may be associated, for example, with the specific shapes of the individual molecules.

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